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UTILITY PATENT APPLICATION TRANSMITTAL
(Large Entity)*(Only for new nonprovisional applications under 37 CFR 1.53(b))*Docket No.
C-572

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Transmitted herewith for filing under 35 U.S.C. 111(a) and 37 C.F.R. 1.53(b) is a new utility patent application for an invention entitled:

LOW VOC WEB OFFSET HEATSET INKS

and invented by:

David Klein, Gary F. Dandreaux, Richard R. Durand, Jr. and Thierry D. FrinaultIf a **CONTINUATION APPLICATION**, check appropriate box and supply the requisite information:☐ Continuation ☐ Divisional ☐ Continuation-in-part (CIP) of prior application No.: _____

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Enclosed are:

Application Elements

1. ☒ Filing fee as calculated and transmitted as described below
2. ☒ Specification having 18 pages and including the following:
 - a. ☒ Descriptive Title of the Invention
 - b. ☐ Cross References to Related Applications *(if applicable)*
 - c. ☐ Statement Regarding Federally-sponsored Research/Development *(if applicable)*
 - d. ☐ Reference to Sequence Listing, a Table, or a Computer Program Listing Appendix
 - e. ☒ Background of the Invention
 - f. ☒ Brief Summary of the Invention
 - g. ☐ Brief Description of the Drawings *(if filed)*
 - h. ☒ Detailed Description
 - i. ☒ Claim(s) as Classified Below
 - j. ☒ Abstract of the Disclosure

UTILITY PATENT APPLICATION TRANSMITTAL
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Docket No.
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Application Elements (Continued)

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- a. ☐ Formal Number of Sheets _____
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- c. ☐ With Power of Attorney ☐ Without Power of Attorney
- d. ☐ DELETION OF INVENTOR(S)
Signed statement attached deleting inventor(s) named in the prior application,
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5. ☐ Incorporation By Reference *(usable if Box 4b is checked)*
The entire disclosure of the prior application, from which a copy of the oath or declaration is supplied under
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6. ☐ CD ROM or CD-R in duplicate, large table or Computer Program (Appendix)
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Accompanying Application Parts

9. ☐ Assignment Papers *(cover sheet & document(s))*
10. ☐ 37 CFR 3.73(B) Statement *(when there is an assignee)*
11. ☐ English Translation Document *(if applicable)*
12. ☐ Information Disclosure Statement/PTO-1449 ☐ Copies of IDS Citations
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Docket No.
C-572

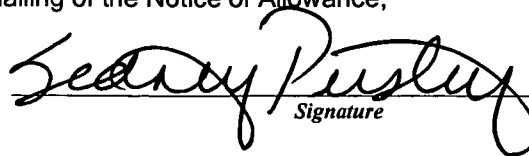
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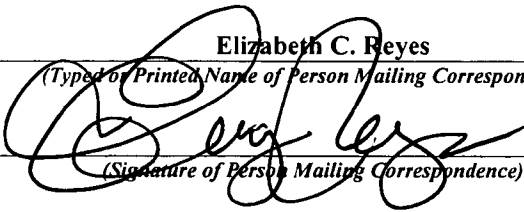
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Signature

Dated: December 31, 2003

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CC:

CERTIFICATE OF MAILING BY "EXPRESS MAIL" (37 CFR 1.10)			Docket No. C-572
Applicant(s): David Klein, et al.			
Serial No.	Filing Date	Examiner	Group Art Unit
Invention: LOW VOC WEB OFFSET HEATSET INKS			
<p>I hereby certify that this <u>Patent Application</u> _____ (Identify type of correspondence)</p> <p>is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 in an envelope addressed to: The Commissioner of Patents and Trademarks, Washington, D.C. 20231-0001 on <u>December 31, 2003</u> (Date)</p> <p><u>Elizabeth C. Reyes</u> (Typed or Printed Name of Person Mailing Correspondence)</p> <p> (Signature of Person Mailing Correspondence)</p> <p><u>EL615315245US</u> ("Express Mail" Mailing Label Number)</p>			
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LOW VOC WEB OFFSET HEATSET INKS

5

FIELD OF THE INVENTION

The invention relates to a web offset heatset ink composition having less than 2% by weight of volatile organic compounds that dries at high speed and contains a latex polymer.

10

BACKGROUND OF THE INVENTION

Historically, lithographic web offset heatset inks contain between 30% and 45% volatile organic compounds (VOC). Besides being detrimental to the environment, VOCs are also flammable and hazardous to the printers who operate the press. Thus, it is desirable to reduce the VOC content in lithographic web offset heatset inks as much as possible. Initial attempts at solving this problem involved the use of chemical reactions that were triggered in a press oven. However, such oven cured ink systems did not have shelf stability.

20

Therefore, a heat setting web offset ink will typically contain the following major components (a) a high molecular weight ink resin to disperse the pigment and also to provide the toughness and gloss the ink requires on drying, (b) solvents to provide the fluidity to the ink before it is placed on the web and dried in an oven, (c) pigment, and (d) other minor components such as gellants, which provide structure to the ink, plasticizers (non volatile solvents), waxes, thickeners, and antioxidants. Conventional heatset inks set or dry by evaporation of the ink oil on heating at 250-300°F, and, to some degree, by penetration of the ink oil into the paper, leaving behind a hard polymeric film.

30

EP 731150 A1 960911 describes rapid thermosetting low VOC web offset lithographic ink systems comprising solid resin, drying oil alkyds, bodied drying oil, vegetable oil, fatty acids, multifunctional unsaturated polyester, reducing agents and transition metal salts of organic acids and may also include an aqueous fountain solution containing peroxides that promote free radical polymerization of the ink. WO96/34922, U.S. Patent 5,431,721, and U.S. Patent 5,545,741, 1996 respectively describe lithographic inks which employ non-volatile solvents, but they set by penetration of the non-volatile solvent into the stock.

Thus, there is still a need to formulate low VOC web offset heatset inks that have good shelf stability and high dry speed.

SUMMARY OF THE INVENTION

The present invention provides a web offset heatset ink composition having less than about 2 wt.% of VOC comprising an aqueous polymer latex dispersed in an ink base that includes:

- (a) an ink resin;
- (b) a non-volatile plasticizer; and
- (c) a pigment.

The present invention also provides a method for increasing drying or setting speed of a web offset heatset ink composition which has less than about 2 wt.% of VOC in which the ink contains the ink base described above and an aqueous polymer latex.

The present invention further provides a method of increasing shelf stability of a web offset heatset ink composition which has less than about 2

wt.% of VOC in which the ink contains the ink base described above and an aqueous polymer latex.

Other objects and advantages of the present invention will become
5 apparent from the following description and appended claims.

DETAILED DESCRIPTION OF THE INVENTION

10 Low VOC (less than about 2% and preferably about 0% VOC) web offset heatset inks which print cleanly on conventional lithographic plates and dry at maximum press speeds of about 1000 ft/minute under typical printing conditions are described. The inks consist of a polymer latex dispersed in an ink base made up of ink resins, a non-volatile plasticizer, and pigment.

Ink Base

15 The ink base includes a high acid number resin as a binder for the pigments. The high acid number resin may have an acid number of about 20 to about 250 and a softening point of between 80 to 200°C. Suitable resins
20 include, but are not limited to, phenolic, maleic, fumaric, pentaerythritol, hydrocarbon resins, and/or mixtures of these groups, rosin resins, rosin salts, tall oil resins, and mixtures thereof. It is preferred that the resin be a phenolic modified rosin ester. A variety of other conventional rosin resins can be used and are readily known to those of ordinary skill in the art.

25 The ink base also includes a non-volatile plasticizer. The plasticizer is selected from the group consisting of tall oil esters, rosin esters, and fatty acid esters. Other suitable plasticizers for use in the ink base, include, but are not
30 limited to alkyds, polyesters, phthallate esters, tallate esters, and mixtures thereof. It is preferred that the non-volatile plasticizer be a tallate ester.

The ink base further includes pigments which include all of those conventionally used and any dye, pigment, filler, or the like, which can be bonded to the resin and permit the resultant resinated pigment to be dispersed, milled, mixed, blended, or dissolved in any conventional manner in forming the final ink composition. The pigment may be in the form of a water-based dispersion, flush, or dry grind. The pigment may be added to the lithographic printing ink composition in either dry powder, flush, presscake, or water based dispersion form.

Polymer Latex

The polymer latex employed in the present invention includes but is not limited to modified acrylics, modified methacrylics, modified styrenes, modified styrene methacrylics, vinyls and mixtures thereof. It is preferred that the polymer latex have an amine functionality, and more preferred that it be an amine functionalized acrylic:styrene copolymer latex.

The increase in stability of the ink composition is due to an acid functionalized protective colloid within the latex itself. It is preferred that the acid functionalized protective colloid be a styrene acrylic resin, such as JONCRYL® 679 manufactured by Johnson Polymer of Racine, WI. The protective colloid prevents the latex particles from interacting with the rest of the ink base and the ink composition until it reaches the oven, thus affording shelf stability of the overall web offset heatset ink composition. The latex containing the protective colloid is termed a supported latex.

The ink composition minus the latex is a viscous oil, and as it is non volatile, it will not dry (or set) under heatsetting conditions. With the latex present, once the ink composition reaches the oven the water and ammonia within it evaporate and heat forces collapse of the glassy latex particles so

that they may blend with the rest of the ink, giving rise to a hard film. The amine groups in the latex can react with acid groups (forming salts) in the high acid number resins upon collapse of the latex in the oven and give rise to an even tougher film. Accordingly, while not being bound by theory, the increase in setting speed is believed to be due to the attraction between the amine functional latex and the acid functional high acid number resins that occurs once the water and ammonia in the polymer latex have been driven off.

The web offset heatset ink may also include water to act as a rheology and/or surface energy modifier of the ink. The water may be an added component or be contributed by one of the other components of the composition such as residual water from a pigment flush, presscake or latex.

The web offset heatset ink may also include additives such as waxes and surfactants which are known in the art.

The web offset heatset printing ink compositions of the present invention are further illustrated by the following non-limiting examples in which all parts and percentages of components are by weight and based on the total weight of the composition, respectively, unless otherwise indicated.

Comparison Example 1

A conventional web offset heatset ink was prepared was prepared from the components indicated below in Table 1 using the an acrylic/styrene latex that does not contain amine functionality.

Table 1

Component	Wt. %
Pigment (Raven 760, Columbia Chemicals Company of Marietta, GA)	10.5
Resin (13.3 wt.% of RP-305, phenolic modified rosin ester, manufactured by Westvaco of Charleston, SC 13.2 wt.% of VSPR-75, a phenolic modified rosin ester manufactured by Akzo Nobel of Chicago, IL)	26.5
Plasticizer (2-ethyl hexyl tallate, Chemol, Greensboro, NC)	34.7
Polymer latex (Lucidene 612, an acrylic:styrene emulsion manufactured by Rohm & Haas of Philadelphia, PA)	28.3
TOTAL	100.0

5 The resins and plasticizer were combined and heated with stirring until molten and homogeneous. The mixture was allowed to cool to room temperature and the pigment was dispersed in the cooled mixture and ground until it became smooth and well dispersed. To the ink base was added the polymer latex and mixed thoroughly.

10 The web offset heatset printing ink was measured for tack on a Go Technology Digital Inkometer, manufactured Go Technology Co. of Loveland, OH at a speed of 1200 rpm at 32°C. The viscosity of the conventional printing ink was also measured at 25°C using an automated Duke Viscometer, manufactured by Duke Technology of Chapmansboro, TN. The conventional
15 printing ink was then printed on a Rochester Institute of Technology's (R.I.T.s) Harris M-1000 web offset heatset press at speeds up to 1200 feet per minute (fpm), web exit temperature of 300°F, and with Rosos KSP 500 M-3 fountain solution (pH of 3.7 and conductivity of 1950 mhos.). The maximum web
20 speed (the speed with which the web operates while still maintaining appropriate drying of the print), tack and viscosity are set forth in Table 2 below.

Table 2

Tack	12.1 gram-meters
Viscosity	210 poise
Maximum web speed	500 feet per minute

Example 2

- 5 An experimental acrylicstyrene latex polymer containing amine functionality and protective colloid was prepared from the components set forth in Table 3 below.

Table 3

	Component	Grams
A	Deionized water	457.1
B	Ammonia (30%, aqueous)	23.4
C	Sodium lauryl sulfate (30% aqueous, RHODOPON UB manufactured by Rhodia, Inc. of Cranbury, NJ).	3.0
D	Polypropylene glycol (POLY G-D1200, manufactured by BASF of Mount Olive, NJ)	9.9
E	Resin (JONCRYL Resin 679, a styrene acrylic resin, Johnson Polymer Racine, WI)	116.5
F	Ammonium persulfate	3.9
G	Deionized water	39.5
H	Dimethylaminoethyl methacrylate	74.0
I	Styrene	262.0
J	2-Ethylhexyl acrylate	0.5
K	Ammonium persulfate	1.0
L	Deionized water	10.0
	TOTAL	1000.0

10

- Ingredients A, B, C, and D were charged and heated to 88°C. When the temperature reached between 75 and 80°C, ingredient E was added over a 20-30 minute period and then the temperature was held for 50-60 minutes at 88°C to dissolve ingredient E. Then, 50% of F & G ingredient mixture was added, followed by 10% of H, I, & J ingredient mixture.

15

Twenty minutes later, the remaining F & G ingredient mixture and H, I,

& J ingredient mixture were added over a period of 1.5 hours and then the heat was maintained for an hour. Thereafter K & L ingredient mixture was added over a period of 20 minutes, and the temperature was held at 88°C for 1 hour, then cooled to room temperature to discharge.

5

The resulting latex emulsion had a pH of 8.28 with solids averaging 46.6% after two readings. The Brookfield viscosity was measured at 154 cP (spindle 3, 60 rpm, 25°C).

10

Example 3

An experimental black web offset heatset printing ink was prepared from the components set forth in Table 4 below.

15

Table 4

Component	Weight Percentage
Pigment (Raven 760, Columbian Chemicals Company of Marietta, GA)	12.0
Resin (11.5 wt.% of RP-305, phenolic modified rosin ester, manufactured by Westvaco of Charleston, SC ; 11.5 wt.% of VSPR-75, a phenolic modified rosin ester manufactured by Akzo Nobel of Chicago, IL)	23.0
Plasticizer (2-ethyl hexyl tallate, Chemol, Greensboro, NC)	31.6
Polymer Latex of Example 2	29.0
Alkali Blue Flush (BASF of Mount Olive, NJ)	2.6
Wax (microcrystalline wax compound, manufactured by Carroll Scientific of McCook, IL)	1.4
Polytetrafluoroethylene compound manufactured by Shamrock Technologies of Dayton, NJ)	0.4
TOTAL	100.0

The resins and plasticizer were combined and heated with stirring until molten and homogeneous. The mixture was allowed to cool to room temperature and the pigment was dispersed in the cooled mixture and ground until it became smooth and well dispersed.

5

To the mixture was added alkali blue flush, wax and PTFE with stirring and mixed thoroughly. The polymer latex of Example 2 was added and mixed thoroughly to form the experimental black web offset heatset printing ink.

10 The experimental black web offset heatset printing ink using the polymer latex of Example 2 was measured for tack 32°C on a Go Technology Digital Inkometer, manufactured Go Technology Co. by Loveland, OH, at a speed of 1200 rpm. The viscosity of the conventional printing ink was also measured using an automated Duke Viscometer at 32°C, manufactured by
15 Duke Technology of Chapmansboro, TN. The printing ink was then printed on Rochester Institute of Technology's (R.I.T.s) Harris M-1000 web offset heatset press at speeds up to 1200 feet per minute (fpm), web exit temperature of 300°F, and with Anchor Premium MEXH IIS fountain solution (pH of 4.3 and conductivity of 1900 mhos.). The maximum web speed, tack
20 and viscosity are set forth in Table 5 below.

Table 5

Tack	8.7 gram-meters
Viscosity	80 poise
Maximum web speed	1000 feet per minute

25

Example 4

An experimental cyan web offset heatset printing ink was prepared from the components set forth in Table 6 below.

30

Table 6

Component	Wt.%
Pigment (Blue Pigment 15:3, manufactured by Sun Chemical Corporation of Ft. Lee, NJ)	12.0
Resin (12.1 wt.% of RP-305, phenolic modified rosin ester, manufactured by Westvaco of Charleston, SC ; 12.1 wt.% of VSPR-75, a phenolic modified rosin ester manufactured by Akzo Nobel of Chicago, IL)	24.2
Plasticizer (2-ethyl hexyl tallate, Chemol, Greensboro, NC)	32.5
Polymer Latex of Example 2	29.0
Wax (microcrystalline wax compound, manufactured by Carroll Scientific of McCook, IL)	1.7
Polytetrafluoroethylene compound manufactured by Shamrock Technologies of Dayton, NJ)	0.6
TOTAL	100.0

5 The resins and plasticizer were combined and heated with stirring until molten and homogeneous. The mixture was allowed to cool to room temperature and the pigment was dispersed in the cooled mixture and ground until it became smooth and well dispersed.

10 To the mixture wax and PTFE was added and mixed through stirring thoroughly. The polymer latex of Example 2 was added and mixed thoroughly to form the experimental cyan web offset heatset printing ink.

15 The experimental cyan web offset heatset printing ink using the polymer latex of Example 2 was measured for tack according to the method set forth in Example 3. The viscosity was measured using an automated Duke Viscometer at 25°C. The printing ink was then printed on a Rochester Institute of Technology's (R.I.T.s) Harris M-1000 web offset heatset press at speeds up to 1200 feet per minute (fpm), web exit temperature of 300°F, and with Anchor Premium MEXH IIS fountain solution (pH of 4.3 and conductivity

of 1900 mhos.). The maximum web speed, tack and viscosity are set forth in Table 7 below.

Table 7

Tack	9.2 gram-meters
Viscosity	130 poise
Maximum web speed	1000 feet per minute

5

Example 5

10 An experimental magenta web offset heatset printing ink was prepared from the components set forth in Table 8 below.

Table 8

Component	Wt. %
Pigment (Red Pigment 57:1, manufactured by Sun Chemical Corporation of Ft. Lee, NJ)	10.2
Resin (12.4 wt.% of RP-305, phenolic modified rosin ester, manufactured by Westvaco of Charleston, SC ; 12.4 wt.% of VSPR-75, a phenolic modified rosin ester manufactured by Akzo Nobel of Chicago, IL)	24.8
Plasticizer (2-ethyl hexyl tallate, Chemol, Greensboro, NC)	33.7
Polymer Latex of Example 2	29.0
Wax (microcrystalline wax compound, manufactured by Carroll Scientific of _ Wax (microcrystalline wax compound, manufactured by Carroll Scientific of McCook, IL)	1.7
Polytetrafluoroethylene compound manufactured by Shamrock Technologies of Dayton, NJ)	0.6
TOTAL	100.0

15

The experimental magenta web offset heatset printing ink was

prepared according to the method described in Example 4. The printing ink was tested according to the measurements set forth in Example 4. The maximum web speed, tack and viscosity are set forth in Table 9 below.

5

Table 9

Tack	10.1 gram-meters
Viscosity	175 poise
Maximum web speed	1600 feet per minute

10

Example 6

An experimental yellow web offset heatset printing ink was prepared from the components set forth in Table 10 below.

15

Table 10

Component	Weight Percentage
Pigment (Yellow Pigment Y-12 manufactured by Sun Chemical Corporation of Ft. Lee, NJ)	10.8
Resin (12.2 wt.% of RP-305, phenolic modified rosin ester, manufactured by Westvaco of Charleston, SC ; 12.2 wt.% of VSPR-75, a phenolic modified rosin ester manufactured by Akzo Nobel of Chicago, IL)	24.4
Plasticizer (2-ethyl hexyl tallate, Chemol, Greensboro, NC)	33.5
Polymer Latex of Example 2	29.0
Wax (microcrystalline wax compound, manufactured by Carroll Scientific of McCook, IL)	1.7
Polytetrafluoroethylene compound manufactured by Shamrock Technologies of Dayton, NJ)	0.6
TOTAL	100.0

The experimental yellow web offset heatset printing ink was prepared according to the method described in Example 4. The printing ink was tested according to the measurements set forth in Example 4. The maximum web speed, tack and viscosity are set forth in Table 11 below.

Table 11

Tack	9.7 gram-meters
Viscosity	150 poise
Maximum web speed	1000 feet per minute

10

The invention has been described in terms of preferred embodiments thereof, but is more broadly applicable as will be understood by those skilled in the art. The scope of the invention is only limited by the following claims.

15

WHAT IS CLAIMED IS:

1. A web offset heatset ink composition having less than about 2 wt.% of volatile organic compounds comprising an aqueous polymer latex dispersed in an ink base that comprises:
 - 5 (a) a resin;
 - (b) a non-volatile plasticizer; and
 - (c) a pigment;
- 10 2. The ink composition of claim 1, wherein said polymer latex is acrylicstyrene copolymer latex.
3. The ink composition of claim 1, wherein said polymer latex comprises a protective colloid which comprises acid functional groups.
- 15 4. The ink composition of claim 3, wherein said protective colloid is an acrylicstyrene polymer.
5. The ink composition of claim 1 wherein said polymer latex has amine functional groups.
- 20 6. The ink composition of claim 1, wherein said resin has acid functional groups.
7. The ink composition of claim 5, wherein said resin is a high acid
25 number resin.
8. The ink composition of claim 1, wherein said non-volatile plasticizer is ethylhexyl tallate.

9. The ink composition of claim 1 having about 1 wt. % volatile organic compounds.

10. A method for increasing drying or setting speed of a web offset heatset ink composition having less than about 2 wt. % of volatile organic compounds and which comprises:

- (a) a resin;
- (b) a non-volatile plasticizer; and
- (c) a pigment;

said method comprising adding to said ink composition an aqueous polymer latex.

11. The ink of claim 10 wherein said polymer latex has amine functional groups.

12. The method of claim 10, wherein said polymer latex is acrylicstyrene copolymer latex.

13. The method of claim 10, wherein said polymer latex comprises a protective colloid which comprises acid functional groups.

14. The method of claim 13, wherein said protective colloid is an acrylicstyrene resin.

15. The method of claim 10, wherein said non-volatile plasticizer is ethylhexyltallate.

16. The method of claim 10, wherein said resin has acid functional groups.

17. The method of claim 10, wherein said resin is a high acid number resin.

18. The method of claim 10, wherein said ink composition contains
5 about 0 wt. % volatile organic compounds.

19. A method of increasing shelf stability of a Web Offset heatset ink composition which has less than about 2 percent by weight of volatile organic compounds (VOC) and which comprises:

- 10 (a) an ink resin;
(b) a non-volatile plasticizer; and
(d) a pigment;

said method comprising adding to said ink composition an aqueous polymer latex and a protective colloid which comprises acid functional groups.

15

20. The method of claim 19 wherein said polymer latex has amine functional groups.

21. The method of claim 19, wherein said polymer latex is
20 acrylicstyrene copolymer latex.

22. The method of claim 19, wherein protective colloid is an acrylicstyrene resin.

23. The method of claim 19, wherein said non-volatile plasticizer is
25 ethylhexyl tallate.

24. The method of claim 19, wherein said resin comprises acid functional groups.

30

25. The method of claim 19, wherein said resin is a high acid number resin.

26. The method of claim 19, wherein said ink composition contains
5 about 0 wt.% of volatile organic compounds.

ABSTRACT

5 A web offset heatset printing ink composition having less than about 2 wt.% of volatile organic compounds containing an aqueous polymer latex dispersed in an ink base of a resin, a non-volatile plasticizer, and a pigment and method for preparing same.